LABORATORY OIEWRVATIONS OF OPTICAL EM1SS1ONS IN THE INTERACTION OF FAST O(^{3}P) ATOMS WITH N$_2$H$_4$ AND HCN

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ABSTRACT

Optical emissions have been detected in collisions of 3-15 eV (laboratory energy) O(^{3}P) atoms with beams of hydrazine (N$_2$H$_4$) and HCN, and with surface-adsorbed N$_2$H$_4$. These species are thought to occur as unspent fuel in the shuttle exhaust. Measurements in gas-phase and surface-adsorbed N$_2$H$_4$ show strong NH (A→X) emission the the range 325-350 run. The threshold for the surface-adsorbed emission is between 3 and 4 eV, and for the beam-beam case at 7 eV. In beam-beam collisions with HCN, one observes strong emissions in the CN A→X and B→X systems in the range 550-850 nm and 300-430 nm, respectively. The threshold for the B→X emission is measured to be 4.6 eV (CM), corresponding to the reaction O(^{3}P) + HCN + 4.1 eV → OH(X) + CN(B).

1.0 INTRODUCTION

The advent of low-earth orbit (LEO) missions and space-borne observing platforms has revealed new phenomena associated with the high translational energies available to the colliding atomic and molecular partners in LEO.   Reaction channels which are normally closed under thermal-energy conditions can be open at the orbital energies. Furthermore, one can compare collision conditions in which the molecular intermediate has, using equipartition of energy, $1/2kT$ (or 0.021 eV at T = 240 K) available to it in each degree of freedom (translational, vibrational, rotational); to one in which the intermediate has enormous energy (5 eV say, or 58000 K) in just the translational degrees of freedom,

The simulation, in the laboratory, of atomic oxygen (AO) effects occurring in LEO poses a considerable experimental challenge. The laboratory simulation is vital, as one would like to perform rapid tests on new materials, or conclusively verify certain LEO observations, without having to propose a long lead-time flight experiment. Moreover, in order to provide credible inputs, the laboratory source must produce the AO as found in 1.EO, with regard to energy range, energy width, quantum state, flux,

and beam purity. Results presented herein were obtained with the JPL AO facility, This facility has provided a number of interesting results on both AO-surface[1,2,3] and AO-gas phase[4] collisions.

The molecular systems reported herein are $O + N_2H_4$ (hydrazine) and O -t HCN (hydrogen cyanide). Both molecular targets are believed to be present as unspent fuels during shuttle rocket motor burns. Their interaction with the AO at the ram energy (7.8 km/s, or 5.0 eV for AO) has led to characteristic optical emissions in LEO observations. These emissions are reproduced in the laboratory, and their dependence on surface material, surface temperature, and collision energy studied.

2.0 EXPERIMENTAL CONSIDERATIONS

A description of the AO source has been given previously [1,2] and only a brief description will be given here. The entire experiment is carried out in a uniform, high-intensity (6T) solenoidal magnetic field. Magnetically-confined electrons having 8.0 eV energy dissociatively attach to NO to form $O^-(^2P)$. The confined O ions are accelerated to the desired final energy (5 eV, say) and are separated from the electrons by trochoidal deflection, The electron in O is then photodetached using all visible lines from a 20 W argon-ion laser in a multiple-pass geometry. The resulting O atom is left exclusively in its ground 3_P electronic state. The O and (undetached) O beams are then directed towards the target, and the O^- ions and detached electrons are reflected by biasing a nearby spherical photon-co] lection mirror negative with respect to the O and electron energies. For the surface studies targets were uncharacterized surfaces of clean Ni and MgF_2 which were continuously exposed to a beam of N_2H_4; or a beam of N_2H_4 or HCN effusing from a 1.0 mm-dia hypodermic needle.

Optical emissions from the targets were collected by a spherical mirror, and focused onto the entrance plane of a double-grating monochromator. Separate spectra of the emissions and backgrounds were recorded by multichannel sealing. The spectral resolution was 4 nm (FWHM).

3.0 RESULTS AND DISCUSSION

3.1 N_2H_4

Shown in Fig. 1 are results for collisions of 5 eV $O(^3P)$ atoms on separate MgF_2 and Ni surfaces with adsorbed N_2H_4. The surface temperatures were held at 300 K. The emissions observed are from the NH A→X transition in the range 325-350 nm. Within present detection limits, no other surface-catalyzed emissions were observed in the wavelength range 300-900 nm. Also, when the surface is removed and replaced by a beam of N_2H_4, no emissions are observed at 5 eV $O(^3P)$ energy. However, when the AO energy is raised to **7.0** eV, the emission in the beam-beam process reappears. This is consistent with recent shuttle observations if one assumes that O atoms in the high-energy tail of the

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Maxwellian distribution, or energetic AO produced by another reaction channel, such as charge exchange or dissociative ionization, are exciting the hydrazine cloud in LEO.
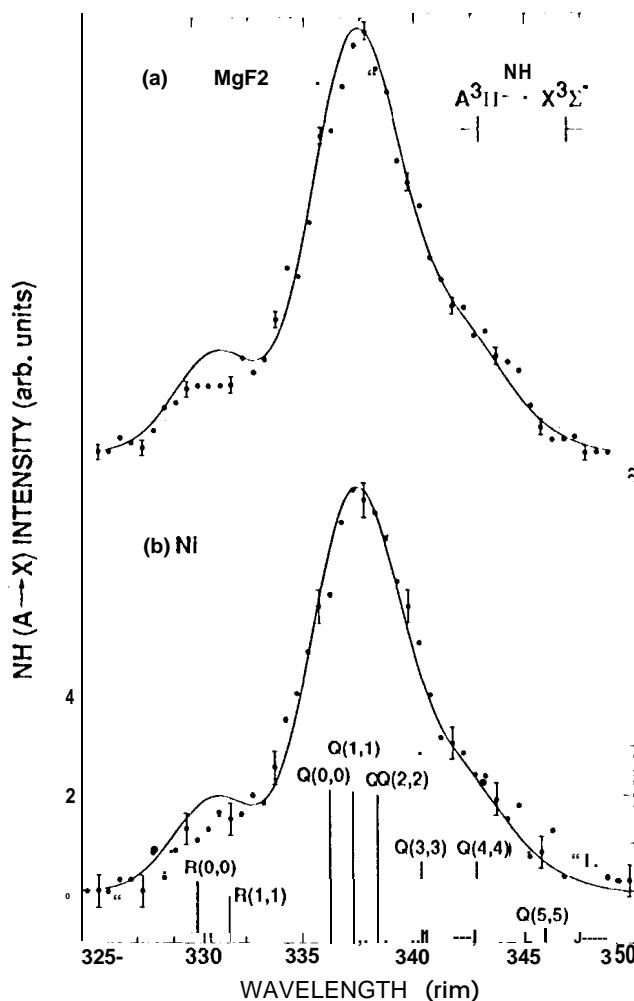

Fig. 1. Emission spectra of the NH A→X transition resulting from 5 eV O(^{3}P) atoms reaction with N_2H_4 adsorbed on (a) MgF_2 and (b) Ni surfaces. Solid line shows convoluted band intensities from spectroscopic data'.

The above results with surface-adsorbed N_2H_4 do not preclude the possibilities that other species may also be present above the surface as "dark" products (in ground or long-lived excited states); or as excited species emitting outside the present spectral range. Work is currently underway at JPL to explore the production of any dark species by mass-spectrometric measurements of surface-desorbed products.

Optical emissions in the A→X and B→X electronic transitions of CN were observed in crossed-beams collisions of AO and HCN[6]. Spectra of the two transitions are shown in Fig. 2 at a laboratory (LAB) energy of 20.0 eV (or center-of-mass CM energy of 12.6 eV). The A→X emission is about a factor of 100 weaker than the B→X. Also shown in Fig, 2 is a simulation of the A→X emission in terms of known energy locations[7] and Franck-Condon factors[8] of the vibrational bands,
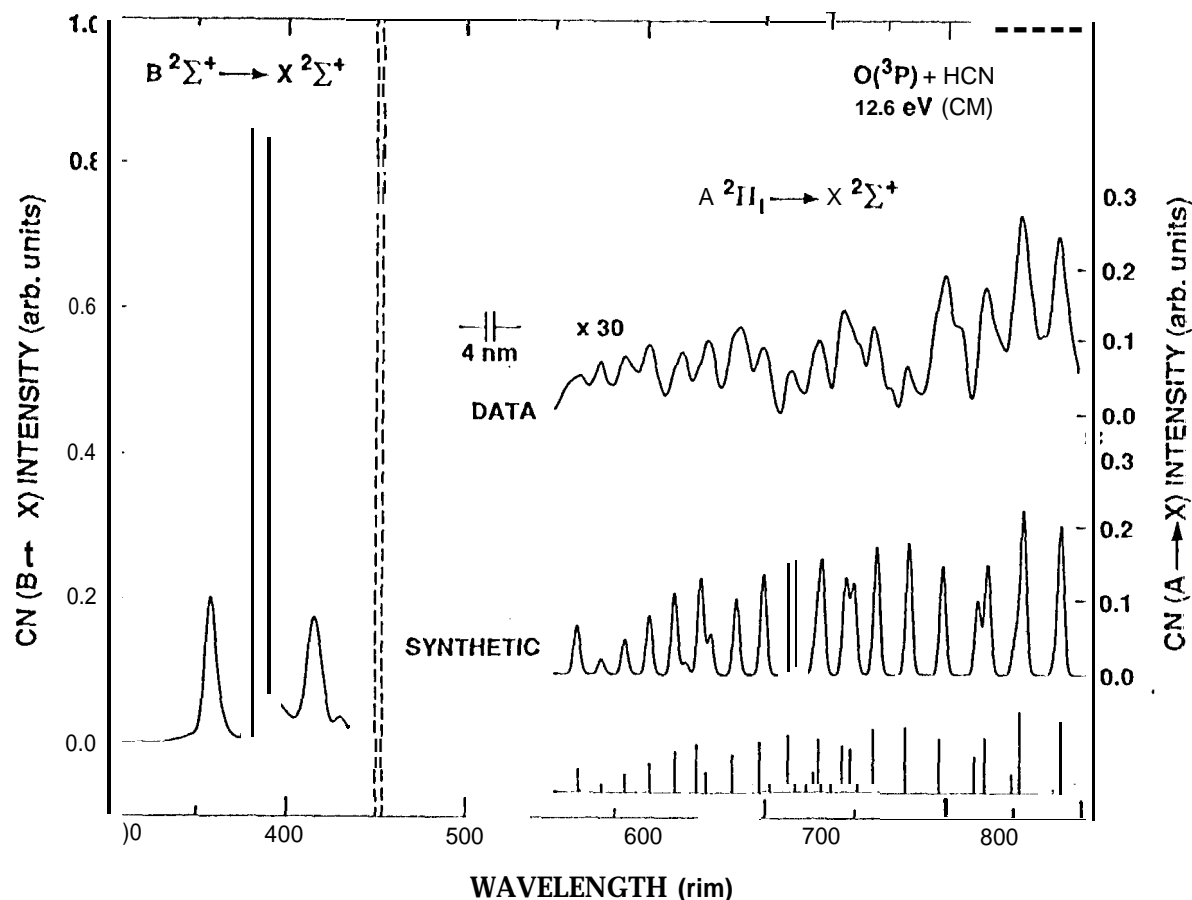

Fig. 2. Measured and simulated spectra of the CN A→X and B→X emission systems at a LAB energy of 20.0 eV (12.6 eV CM energy).

[6]O.J. Orient, A. Chutjian, K.E. Martus and E. Murad, *Phys.* Rev. *A*, in press.

[7]K. P. Hu ber and G. H erzberg, *Molecular Spectra and Molecular Structure W. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979) p. 154,

[8]H. Lavendy, G. Gandara and J ,M. Robbe, *J. Molec. Spectrosc. 106,* 395 (1984).

The B→X transition is studied in more detail, and results are given in Fig. 3. Here, one finds strong contributions from the three main sequences Av = O, + 1 and -1. A nonlocal thermodynamic equilibrium (NLTE) code was used to characterize the emitting B state in terms of separate vibrational T, and rotational T_r temperatures Results (Fig. 3) are given for the values T, = 7000 K (0.603 eV) and T_r = 2000 K (O. 172 eV). The agreement between experiment and simulation is within the combined uncertainties,
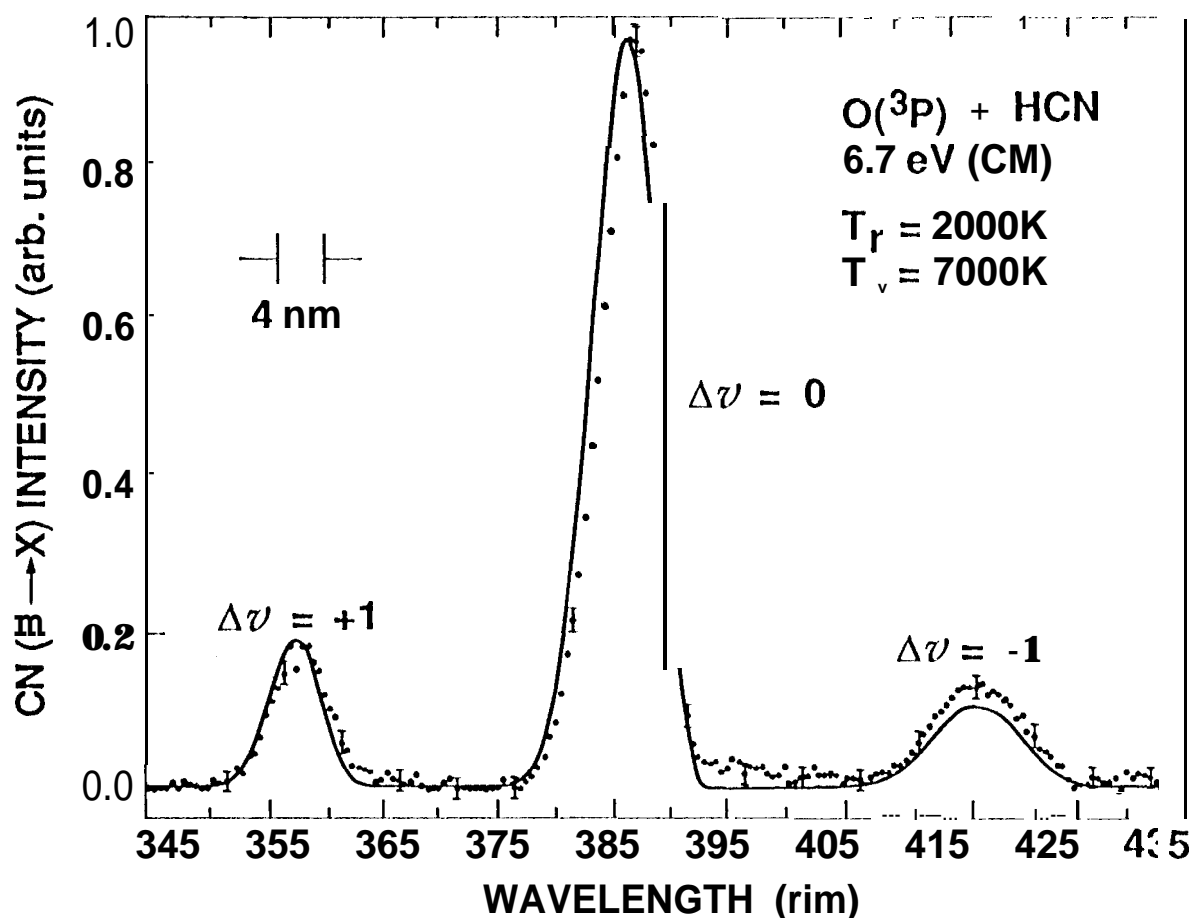

Fig. 3. Measured (●) and simulated (- -) spectra of the CN B→X emission system at the indicated CM energy. The Av = O, + 1 and -1 vibrational sequences are shown.

Central to specifying the appropriate reaction channel is the threshold energy of that channel. With the monchromator wavelength fixed at the peak of the Av = O sequence in the B→X transitions (387 rim), the emission intensity was monitored as a function of the O(^{3}P) energy. Results of this optical excitation-function measurement are shown in Fig. 4. The energy distribution of the O(^{3}P) atoms was

[9]A. Berk, 1.. S. Bernstein, S.C. Richtsmeier, J.W. Cox and M.W. Slack, "UV-VIS NLTE Plume Spectral Emission Model" (presented at *IRIS Specialty Group on Targets, Backgrounds and Discrimination Symposium*, Monterey, CA January 1990, unpublished).

measured in a separate retarding-potential difference experiment on the precursor $O^-(^2P)$ ions. By unfolding this energy distribution from measurements (Fig. **4**) one obtains an energy threshold of 7.4 $\pm$ 0.8 eV (LAB) or 4.6 $\pm$ 0.5 eV (CM) This is very likely an upper limit, since thresholds generally trend to lower values with any increase in instrumental signal/background.
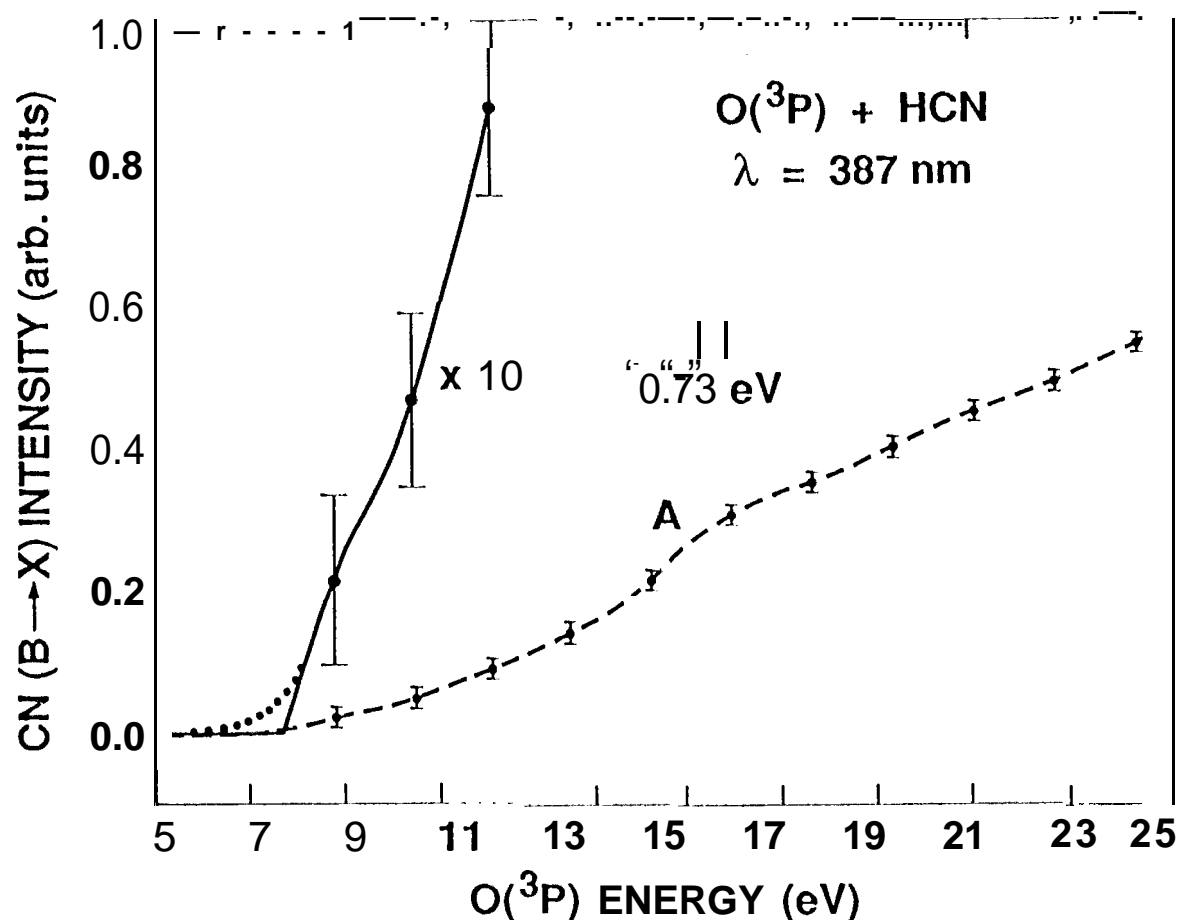

Fig. **4.** Optical excitation function of the B→X emission at 387 nm as a function of $O(^3P)$ LAB energy (curve A). The excitation function has been deconvoluted from the energy distribution of the $O(^3P)$ beam itself, and the excitation threshold is measured to be 7.4 $\pm$ 0.8 eV (LAB, from Curve A x 10). Dotted portion (*..) is the intensity without deconvolution.

It is possible from this measurement to   determine that the reaction channel is given by

$$O(^3P) + HCN(\widetilde{X}) + 4.1 \ eV \rightarrow OH(X) + CN(B) \tag{1}$$
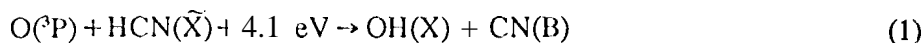
From the enthalpies of reaction the energy required for reaction and excitation to the B-level at 387 nm is 5.25 (H---CN bond energy) -4.35 (O---H bond energy) + 3.20 (B-state energy) = 4.10 eV (CM) or 6.53 (LAB). This is in good agreement with the measurement (4.6 $\pm$ 0.5 eV CM), especially with the caveat above.

The combination of LEO observations and laboratory simulation, with an AO source whose characteristics are determined, lends itself to studying A O-induced phenomena such as photon emission, creation of "dark" products from surfaces, and erosion of surfaces and optical components. Possibilities also exist for studying synergistic phenomena, such as AO-UV effects. The fact that one can now carry out the major study effort in the laboratory means that important screenings and simulations can take place prior to requesting a flight opportunity.

4.0 ACKNOWLEDGEMENTS